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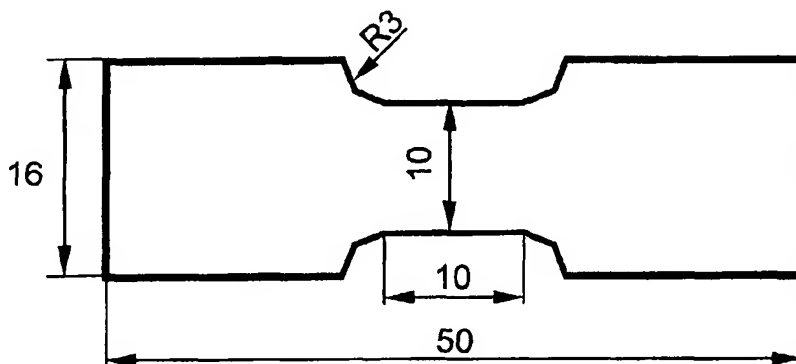
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(54) Title: **AQUEOUS HETEROPOLYMER DISPERSION FOR MANUFACTURING COATINGS AND PROCESS OF ITS PRODUCTION**



(57) Abstract: An aqueous heteropolymer dispersion for manufacturing coatings, particles of the dispersion comprising copolymers that include acrylic monomer units and comprising a core and at least one outer shell, wherein: the particles comprise the core, an intermediate shell and an outer shell; a core copolymer is a copolymer of (meth)acrylate ester, or a mixture of said esters, and ethylenically unsaturated monomer containing two or three C=C bonds, and, optionally, an ethylenically unsaturated monomer containing carboxylic groups, the core copolymer is a copolymer of methacrylate ester, or a mixture of said esters, an ethylenically unsaturated monomer containing two or three C=C bonds, and, optionally, an ethylenically unsaturated monomer containing carboxylic groups, the intermediate shell copolymer having a glass transition temperature of 50 to 85 °C; an outer shell copolymer is a copolymer of methacrylate ester, or a mixture of said esters, and an ethylenically unsaturated monomer containing carboxylic groups, the outer shell copolymer having a glass transition temperature of 25 to 70 °C; and wherein the weight parts of the core, intermediate shell and outer shell are, respectively, 60-75, 7.5-20, and 10-22.5; and the average size of the particles is of 50 to 220 nanometers.



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AQUEOUS HETEROPOLYMER DISPERSION FOR MANUFACTURING COATINGS AND PROCESS OF ITS PRODUCTION

This invention relates to aqueous heteropolymer dispersions which are used for manufacturing coatings, specifically, transparent, high impact coatings for glass articles. Such dispersions can be used for producing glass objects, such as lighting devices, display screens, glass fibers, etc., which do not release splinters when broken. The process of forming a coating film on glass articles involves dipping, spraying, etc., using an aqueous polymer wherein use of an aqueous dispersion is preferable with respect to ease of application and environmental protection.

Various aqueous polymer dispersions or their compositions are known to be useful for producing coatings on glass surfaces.

US Patent 4,263,362 (1981) discloses an aqueous composition comprising an elastomer latex, plasticizer and minor quantities of other ingredients. The composition contains a latex based on a polybutadiene or carboxylated styrene-butadiene copolymer. The coatings produced from these polymers are tacky and not hard due to the low glass transition temperature of these polymers, especially in the presence of plasticizers.

US Patent 3,919,440 (1975) discloses a composition including latex based on a copolymer of butadiene, unsaturated carboxylic acid and a vinyl compound. Coatings made using this composition have insufficient heat- and light-resistance as well as low strength; as is apparent since glass articles coated with it fail, even with coatings as thick as 145–250 μ .

Aqueous polymer compositions including latex based on polybutadiene or styrene-butadiene-vinylpyridine copolymers are disclosed in US Patents 4,060,658 (1977) and 3,853,605 (1974). These compositions contain resorcinol-formaldehyde resins ensuring the formation of a strong and hard coating. However, the high C-C double bond content of said polymers renders coatings made from them insufficiently resistant to atmospheric and chemical influence.

Polymeric compositions based on acrylic monomers are more suitable for coating glass articles. For instance, US Patent 3,970,628 (1976) discloses aqueous dispersions of thermosetting compositions which include acrylic polymers and epoxy resins. The dispersions might be usable for glass coating, but the patent includes no information about the strength of the coating.

US Patents 3,944,100 (1976) and 4,098,934 (1978) disclose compositions including acrylic latex, for example, a latex of acrylonitrile-ethyl acrylate copolymer, cross-linking agent and thickening agent. Using these compositions, or a composition according to US Patent 3,970,628, for coating glass requires high curing temperatures.

5 Aqueous acrylic polymer dispersions for coating glass fibers are disclosed in US Patent 5,827,612 (1998). Forming coatings using these dispersions includes the following steps:

1. applying a first acrylic polymer dispersion to the surface of glass fibers using known methods;
- 10 2. drying the first polymer layer at ambient or elevated temperature;
3. applying a second acrylic polymer dispersion having a composition different from the first polymer to the surface of the first polymer layer by dipping the article into the second dispersion;
4. drying the second polymer layer.

15 Multistage formation of the coating is a disadvantage of these dispersions. It would be preferable to use an aqueous polymer composition which would enable the formation of a polymer coating by a single application step followed by drying.

German Patent Application 2,424,329 (1974) discloses aqueous polymer compositions based on an acrylic polymer dispersion, for example, Hycar 2679, with the addition
20 of a 1 percent solution of polyacrylamide Polyhall 295 for thickening the dispersion and ensuring the required thickness of the polymer film. The composition forms a coating for glass articles which coating has improved mechanical properties and ensures that when a glass article is broken, it does not release splinters, such coating as well as the coated glass article being referred to hereinafter as "non-splintered". The coating is formed by dipping
25 a glass article into the polymer dispersion followed by preliminary drying at an ambient temperature and final hardening at a temperature of 232°C for 4 minutes. The impact strength of the coating is estimated by breaking the article under certain conditions and counting the number of splinters formed. Uncoated glass articles give 120-155 splinters, depending on type of article (Table 1 from German Patent Application 2,424,329). The
30 number of splinters formed by breaking a coated glass article is reduced to 18-43 (Examples F, G, H of the said Table 1), depending on the thickness of coating film. Thus, a glass article with said acrylic polymer coating is not a non-splintered article. The impact strength of a glass article is improved, and the article becomes non-splintered, if tetra-i.-

propyl titanate (a moistener) and then polyethylene emulsion SC-100 is applied to the surface of the glass article before applying the acrylic polymer dispersion. (Example K from said Table 1).

5 This composition disadvantageously requires a multistage coating process. At least, three successive operations of applying followed by drying are required to produce a non-splintered glass article.

As a rule, coatings including various above described latex systems are single-phase polymeric systems which can contain hard inclusions of cured thermosetting resins. Usage of microheterogenous polymeric systems for producing coatings with significant
10 impact strength is considered to be more preferable.

An aqueous heteropolymer dispersion for manufacturing coatings is disclosed in US Patent 4,009,317 (1977), particles of the dispersion comprising copolymers which include acrylic monomer units and consisting of a core and one outer shell. This dispersion is nearest to the dispersion of the invention with respect of its technical essence. An aqueous
15 polymer composition prepared based on said known dispersion was used for single-stage coating of glass fibers. It might be possible that the coating can be optically transparent and have high impact strength, due to the use of acrylic polymers for the formation of the core and the shell, if there would be an adequate quantity of shell polymer in the composition. However, transparency and impact strength of coatings are not mentioned in
20 the specification of US Patent 4,009,317. A low shell polymer glass transition temperature and the inclusion of various additives into composition, such as paraffin, wax, cationic lubricant, etc., are disadvantages of coatings based on the aqueous polymer composition disclosed in US Patent 4,009,317. Both factors increase coating tackiness and prevent adequate surface hardness.

25 US Patents 4,469,825 (1984) and 5,157,084 (1992) disclose processes for producing aqueous heteropolymer dispersions useful in the manufacturing coatings, particles of the dispersion comprising copolymers that include acrylic monomer units, by multistage emulsion copolymerization of said monomers in the presence of anionic surfactant and water soluble free-radical initiator.

30 A process for producing an aqueous heteropolymer dispersion for manufacturing coatings for glass fibers is known from US Patent 4,009,317 (1977). Particles of the dispersion comprise copolymers which include acrylic monomer units and consist of a core and one outer shell, the process including two-stage emulsion copolymerization compris-

ing successive stages of emulsion copolymerization of monomers for the formation of the core and outer shell at a temperature less than 100°C in the presence of a water soluble free-radical initiator and an anionic surfactant. Said process is nearest to the process of the invention in respect of its technical essence. According to this process, a core of particles is produced by emulsion polymerization of alkyl methacrylates, such as, methyl methacrylate. Then, emulsion polymerization of other monomers, such as alkyl acrylates, is carried out in the presence of the dispersion produced in the preceding stage, forming a polymer shell which shell has a glass transition temperature of 10°C or less. The resulting polymeric dispersion is not directly used for coating, but an emulsion of some additives, such as paraffin, wax, etc., is first produced and then mixed with the dispersion, so that process of producing a final composition for coatings includes at least three processes, that is, heteropolymer dispersion production, emulsion production and mixing two components.

The present invention provides a technical result which simplifies the technology of producing high impact polymer coatings on glass articles due to the use of the aqueous polymer dispersion of the invention that is produced by the process according to the invention. Said dispersion together with the process for its production provide a high impact non-splintered coating by a single applying to a glass article followed by drying.

Said technical result is achieved by using an aqueous heteropolymer dispersion of the invention for manufacturing coatings, specifically, transparent high impact coatings on glass articles, particles of the dispersion comprising copolymers, which include acrylic monomer units, and consisting of a core and, at least, one outer shell, wherein the particles comprise the core, an intermediate shell and an outer shell. The core copolymer is a copolymer of (meth)acrylate ester, or a mixture of said esters, at least one ethylenically unsaturated monomer containing two or three C=C bonds, and, optionally, at least one ethylenically unsaturated monomer containing carboxylic groups, the copolymer having a glass transition temperature of less than 7°C. The intermediate shell copolymer is a copolymer of methacrylate ester, or a mixture of said esters, at least one ethylenically unsaturated monomer containing two or three C=C bonds, and, optionally, at least one ethylenically unsaturated monomer containing carboxylic groups, the copolymer having a glass transition temperature of 50 to 85°C. The outer shell copolymer is a copolymer of methacrylate ester, or a mixture of said esters, and at least one ethylenically unsaturated monomer containing carboxylic groups, the copolymer having a glass transition tempera-

ture of 25 to 70°C The weight parts of core, intermediate shell and outer shell are 60-75, 7.5-20, and 10-22.5, respectively, and the average size of the particles is of 50 to 220 nanometers.

As used herein, the term “(meth)” as used in, for example, “(meth)acrylate” indicates that the relevant methyl group is optional. For example, the term “(meth)acrylate” is generic to the corresponding methacrylate and acrylate.

Preferably, the (meth)acrylate ester is a compound of general formula $\text{CH}_2=\text{C}(\text{R})-\text{C}(\text{O})\text{OR}_1$, where R is H or CH_3 , and R_1 is C_1 - C_{18} alkyl. Preferred examples of these esters include, compounds selected from the group including methyl acrylate, ethyl acrylate, n-butyl acrylate, iso-butyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, methyl methacrylate and ethyl methacrylate.

The ethylenically unsaturated monomer containing two or three $\text{C}=\text{C}$ bonds functions as a crosslinker. Preferred examples of these include compounds selected from the group including: di(meth)acrylate esters of ethylene glycol, diethylene glycol, triethylene glycol; allyl (meth)acrylate; trimethylolpropane trimethacrylate; triallyl cyanurate; divinylbenzene.

The ethylenically unsaturated monomer containing carboxylic groups is, preferably, a compound selected from the group including acrylic acid or its α - C_1 - C_5 alkyl derivatives, as well as maleic acid, fumaric acid, itaconic acid or C_1 - C_4 alkyl monoesters thereof.

Preferably, the core copolymer is a copolymer of (meth)acrylate ester or a mixture of said esters, di(meth)acrylate ester, and, optionally, (meth)acrylic acid, the copolymer containing 0.1 to 0.5 wt. percent of di(meth)acrylate ester units and 0 to 5 wt. percent of (meth)acrylic acid units. The intermediate shell copolymer preferably is a copolymer of methacrylate ester or a mixture of said esters, di(meth)acrylate ester, and, optionally, (meth)acrylic acid, the copolymer containing 0.5 to 2.0 wt. percent of di(meth)acrylate ester units and 0 to 7.5 wt. percent of (meth)acrylic acid units. The outer shell copolymer preferably is a copolymer of methacrylate ester or a mixture of said esters, and (meth)acrylic acid, the copolymer containing 7.5 to 10.0 wt. percent of (meth)acrylic acid units.

A process for producing an aqueous heteropolymer dispersion of the invention useful for manufacturing coatings is proposed, particles of the dispersion comprising copolymers which include acrylic monomer units and consisting of a core and at least one outer

shell, the process including multistage emulsion copolymerization comprising successive stages of emulsion copolymerization of monomers for the formation of the core and shell at a temperature less than 100°C in the presence of a water soluble free radical initiator and an anionic surfactant. The stage of producing the core copolymer preferably is divided into two steps, the first step including emulsion copolymerization in the presence of the initiator and the anionic surfactant by batch feeding 10 to 30 percent of the whole quantity of core monomers to form an initial latex, the second step including gradual addition of the remaining amount of core monomers, optionally as an emulsion stabilized with anionic surfactant, to the initial latex formed in the first step. The stage of producing intermediate shell copolymer is carried out by feeding an intermediate shell monomer mixture into the core copolymer dispersion in the presence of a suitable amount of initiator. The stage of producing an outer shell copolymer is carried out by emulsion copolymerization of outer shell monomers in the presence of the dispersion produced in the preceding stage, the outer shell monomers being added either in two equal portions after addition of aqueous solutions of the initiator and anionic surfactant, or fed as an aqueous monomer emulsion stabilized by anionic surfactant with simultaneous feeding of the aqueous initiator solution which optionally contains dissolved anionic surfactant. After completing the process, an aqueous solution of ammonia, or volatile aliphatic amine, or water soluble bivalent metal hydroxide or salt, is added to the dispersion, an amount of from 0.1 to 1.0 mole per mole of carboxylic group units of said ethylenically unsaturated monomer containing carboxylic groups.

The process of the invention includes a stage for producing core copolymer in two steps. First, from 10 to 30 weight percent of the bulk of monomers forming a core copolymer is introduced into an aqueous phase containing dissolved initiator and anionic surfactant. The mixture is polymerized to produce a primary latex. Then, the rest of monomer mixture is fed to the primary latex, preferably as an emulsion stabilized by anionic surfactant. An alkyl acrylate or its mixture with an alkyl methacrylate is preferred in producing core copolymer. Preferably, a weight ratio of alkyl acrylate and alkyl methacrylate is employed such that the glass transition temperature of the core copolymer is less than 7°C, preferably, from -54 to -25°C.

A stage of producing an intermediate shell copolymer can be carried out by feeding a monomer mixture to the core copolymer dispersion. An aqueous solution of initiator preferably is added to the core copolymer dispersion before introducing said monomer

mixture. A mixture of two different alkyl methacrylates can be used at this stage, their weight ratio preferably providing an intermediate shell polymer glass transition temperature of from 50-85°C, preferably 50-70°C. The intermediate shell copolymer can be also produced in two steps with different compositions of monomer mixtures, an aqueous solution of initiator and anionic surfactant being introduced at the second step simultaneously with the monomer mixture.

A stage of producing an outer shell copolymer preferably is carried out by emulsion copolymerization of outer shell monomers in the presence of the dispersion produced in the previous stage, the dispersion containing particles consisting of the core and intermediate shell. The monomers advantageously can be introduced in two equal portions. In this case, aqueous solutions of the initiator and anionic surfactant preferably are introduced before adding outer shell monomers. It is preferred to feed the outer shell monomer mixture as an aqueous emulsion stabilized by anionic surfactant, while simultaneously feeding an aqueous solution of initiator and anionic surfactant. A sole methacrylate or a mixture of two different methacrylates can be used at this stage, their weight ratio providing a shell polymer glass transition temperature of from 25-70°C, preferably 30-60°C.

An aqueous solution of ammonia, volatile aliphatic amine, such as trimethylamine, diethylamine, triethylamine, diethylethanolamine, or water soluble bivalent metal hydroxide or salt, for example, barium or zinc, preferably, barium hydroxide, zinc acetate or its ammonia complex, is added to the aqueous heteropolymer dispersion after completing the polymerization process. A quantity of the said agent is of 0.1 to 1 mole per 1 mole of carboxylic group units of the ethylenically unsaturated monomer containing carboxylic groups. Said agent addition results in at least partial neutralization of the carboxylic groups of said ethylene unsaturated monomer. Moreover, a bivalent metal compound not only neutralizes carboxylic groups but also acts as a cross-linking agent increasing the surface hardness of the coating. A non-ionic surfactant such as, for example, an ethoxylated aliphatic alcohol, can be added to the dispersion before introducing the bivalent metal compound. If used, the quantity of said surfactant preferably is from 0.1 to 1 wt. percent based on the solids of the dispersion..

Conversion of the monomers to copolymer is essentially complete at every stage of the process, that is, a composition of copolymer formed corresponds with the composition of the monomer mixture. This preferably is accomplished by selecting appropriate values of initiator and anionic surfactant concentration and process duration including, for exam-

ple, maintaining the polymer dispersion at a reaction temperature for 30 minutes after completing the introduction of reactants to the reactor. It is preferred to use 0.3 to 0.4 percent of water soluble initiator and 0.2 to 2 percent of anionic surfactant based on monomer weight when producing the core copolymer, said quantities being, respectively, 0.3 to 0.9 percent and 0 to 0.5 percent based on monomer weight when producing the intermediate shell copolymer, and 0.3 to 1.2 percent and 0.3 to 3.0 percent based on monomer weight when producing the outer shell copolymer.

Known water-soluble compounds, including persulfates such as ammonium, sodium, and potassium persulfate, can be used as initiators for emulsion polymerization.

10 Sodium C₁₂-C₁₈ alkyl sulfonates, such as Elfan OS-46 (C₁₄-C₁₆ alkyl mixture, produced by Akzo Nobel) as well as sodium C₁₀-C₁₈ alkylaryl sulfonates or sodium C₁₂-C₁₈ alkyl sulfates are examples of preferred anionic surfactants.

It is very important to maintain the above-described monomer composition limits when feeding monomer during the polymerization process. Deviation from the prescribed limits can be expected to produce tacky and/or low impact coatings.

Aqueous heteropolymer dispersions produced according to the invention have the following characteristics:

- solids: 36-50 wt. percent,
- particle size: 50-220 nanometers,
- 20 - pH: 7-8.4, using ammonia, or 2.2-2.3, using zinc acetate,
- viscosity: 30-53 s (flow time of VZ-4 viscometer).

Coatings based on dispersions produced according to the invention are characterized by high transmittance (integral light transmission 91-92 percent), hardness and impact strength. Glass articles with this coating are truly non-splintered because all splinters are maintained within a polymer shell when the article is broken.

The methods for determining the characteristics of the aqueous heteropolymer dispersions and coatings prepared therefrom are described below:

1. The pH of the dispersions is determined using universal ionometer EV-74.
2. Particle size is determined using the well-known technique of light scattering using a diluted dispersion based on obtaining a logarithmic dependence of optical density vs. wave length (V.I.Klenin et al. Characteristic Functions of Light Diffusion in Dispersed Systems, Saratov University Edition, 1977, 177pp.)

3. Solids content of the dispersion is determined with the gravimetric method of Russian Standard GOST 25709-83.

4. Copolymer adhesion is determined with the method of 180° peeling test from a glass plate.

5. Coating hardness is determined with a Pendulum damping test according to Russian Standard GOST 5233-89 (pendulum weight 120±1 g, pendulum length 500±1 mm, diameter of stainless steel ball 7.938 mm). Relative hardness H is calculated according to the equation:

$$H = t/t_1,$$

where t is the time for damping from a 5° displacement to a 2° displacement on the coating prepared on glass substrate, t₁ is the time for damping from a 5° displacement to a 2° displacement on the same glass substrate free of the coating.

6. Relative viscosity of the dispersion is determined with a cup-type viscometer VZ-4 according to Russian Standard GOST 8420-74 (the cup volume is 120±1 cm³, the nozzle diameter is 4 mm).

7. Light transmission is determined according to Russian Standard GOST 15875-80 with a photometer.

8. The tackiness of the coating is determined with a qualitative test: a sheet of standard writing paper is put on a coated smooth glass surface and pressed to the surface with a pressure of 0.005 MPa, the thickness of coating being not less than 100 micrometers. The coating is not tacky if no traces of paper adhere to the coating.

9. The glass transition temperature T_{gt} of the copolymer is calculated using the Fox equation:

$$\frac{1}{T_{gt}} = \frac{q_1}{T_{gt1}} + \frac{q_2}{T_{gt2}} + \frac{q_3}{T_{gt3}} + \frac{q_4}{T_{gt4}}$$

where q_n is mass fraction of the monomer n,

T_{gt}—glass transition temperature of the polymer n. The source for homopolymer T_g data was “Polymer Chemistry Handbook” (Spravochnik po khimiyi polimerov) of

Yu.S.Lipatov, A.E.Nesterov, T.M.Gritsenko, R.A.Veselovsky issued by "Naukova Dumka" Publ., Kiev, , 218-228 (1971). It is noted that the correcting increment ΔT_g was added to the T_g of copolymers calculated using the Fox equation when a cross-linking monomer was included in the formulation, the increment being calculated from the empirical equation

$$\Delta T_g = 3,9.104 / M_c$$

where M_c is molecular weight of the chain segments between the bonds of cross-linking (calculated from the formulation). The above empirical equation is taken from "Polymer Encyclopedia" (Entsiklopediya polimerov) issued by "Sovetskaya Entsiklopediya" Publ., Moscow, vol. 3 , p. 657 (1977).

10. The minimum film-formation temperature (MFFT) is determined as a boundary between the continuous and discrete part of the film during formation of the coating on the horizontal surface of an apparatus having a linear temperature gradient.

11. Film impact strength is determined with a suitable method developed therefor. A hitting pendulum according to DIN 53448 is used for the test. A sample of the film as shown in Fig. 1 and of 0.3 to 0.8 mm thickness is fixed with two clamps on the base of an apparatus for measuring impact strength, one of the clamps being attached rigidly, another being movable. A II-shaped hammer of the pendulum hits the movable clamp in a transverse flange, the movable clamp being moved, and the sample being broken down. The twin-blade hammer is designed to simultaneously strike both edges of the sample holder on either side of the sample test strip. The clamps for fixing the sample are of a great importance. The sample could move during the test if it is loosely secured, a friction loss taking place. Another energy loss determined by a control test is the work of withdrawal of the movable clamp with the remainder of the sample. The Impact tensile strength Q_t (kJ/m^2) is calculated by the equation:

$$Q_t = \frac{A - A_0}{b \times h} \times 10^3$$

where A is energy of sample failure (J), A_0 is energy of clamp withdrawal (J), b is sample width (mm) and h is sample thickness (mm).

12. The impact strength of glass articles coated with the dispersion of the present invention is determined by destruction of thick-wall glass pipes (300 mm length, 36 mm diameter, 1.5 mm wall thickness) with coatings of thickness not less than 100 micrometer, when falling from the height of 1.5 m to a massive base of concrete. A coating passes the test if the polymer shell is not torn and/or peeled during glass destruction and article deformation, and all the splinters are maintained within the polymer shell. The glass pipes are coated by dipping them into the dispersion followed by 2 hours drying at the temperature of 90°.

The invention is illustrated with the Examples 1 to 13 that are given below. All the Examples describe a three-stage process of producing a dispersion with particles having a core, intermediate shell and outer shell. All parts and percentages are by weight unless otherwise indicated.

Example 1.

Stage 1.

45 g of demineralized water with dissolved 0.9 g of anionic surfactant Elfan OS-46 (sodium C₁₄-C₁₆ alkyl sulfonate, product of Akzo Nobel) was fed into 0.5 l reactor. The reactor contents were blown with nitrogen and heated to 80°C. A monomer mixture containing 22.17 g of n-butyl acrylate (BA) and 0.07 g of ethylene glycol dimethacrylate (EGDM) was fed into the reactor, 0.13 g of ammonium persulfate (AP) dissolved in 10 g of water was added after 5-min. stirring, and a primary copolymerization process was carried out for 30 min. to form a primary dispersion. A solution of 0.13 g AP in 5 g of water was added to the primary dispersion, the dispersion was stirred for 5 min., and a separately prepared emulsion including 66.5 g of BA, 0.20g of EGDM, 2.71g of a 37 percent aqueous solution of Elfan OS-46 and 28 g of water was added over 120 minutes at the rate of 0.812 g/min. After completing the addition, the dispersion was stirred for 30 min. at the temperature of 80°C.

Stage 2

0.16 g of AP dissolved in 3 g of water was added to the dispersion prepared in Stage 1. The mixture was stirred for 5 min. A monomer mixture containing 5.32 g of methyl methacrylate (MMA), 11.44 g of n-butyl methacrylate (BMA), 0.88 g of methacrylic acid (MAc) and 0.09 g of EGDM, was fed over 60 min. at the rate of 0.296

g/min. After the feeding was completed, the dispersion was stirred for 30 min. at a temperature of 80°C.

Stage 3

0.05 g of AP dissolved in 9 g of water was added to the dispersion formed in Stage
5 2. The mixture was stirred for 5 min. A separately prepared emulsion including 1.33 g of MMA, 23.34 g of BMA, 2.0g of MAc, 1.3 g of a 37 percent aqueous solution of Elfan OS-46 and 12 g of water, was fed over 180 min. at the rate of 0.222 g/min. After 90 min. of feeding, a solution of 0.05 g AP in 9 g of water was added. The dispersion was stirred for 30 minutes at a temperature of 80°C after the monomer feed was completed. The resulting
10 dispersion contained 0.01 percent of residual BMA, and no detectable BA, MAc, MMA or EGDM. The dispersion was cooled and neutralized with 1.61 g of 24.5 percent aqueous ammonia. The total duration of the process was 500 minutes.

Table 1 includes the feeding ratios for all the Examples. Table 2 includes data on the composition and properties of the dispersions produced according to the Examples.

15

Example 2.

Stage 1 was carried out analogous to that of the Example 1.

Stage 2

0.09 g of AP dissolved in 9.9 g of water was added to the dispersion prepared in
20 Stage 1. The dispersion was stirred for 5 minutes. A monomer mixture, containing 5.60 g of MMA, 3.61 g of BMA, 0.76 g of MAc and 0.20 g of EGDM, was fed over 60 min. at the rate of 0.1695 g/min. After completing the addition, the dispersion was stirred for 30 min. at a temperature of 80°C.

Stage 3

25 A separately prepared emulsion including 14.26 g of MMA, 13.33 g of BMA, 2.24 g of MAc, 1.21 g of a 37 percent aqueous solution of Elfan OS-46 and 10 g of water was fed over 240 min. at the rate of 0.1710 g/min. to the dispersion prepared in Stage 2. Simultaneously, an aqueous phase including 0.09g of AP, 0.20 g of a 37 percent aqueous solution of Elfan OS-46 and 12.2 g of water, was fed at the rate of 0.0520 g/min. After the
30 feed of the emulsion and aqueous phase was completed, the dispersion was stirred for 30 min. at a temperature of 80°C. The dispersion was cooled and neutralized with 1.81 g of 24.5 percent aqueous ammonia. The total duration of the process was 555 min.

Example 3.

A dispersion was produced as in Example 1 but the feed ratio was changed, the polymerization temperature was 90°C, and the total process duration was 470 min.

5 Example 4.

A dispersion was produced as in Example 1 but the feed ratio was changed, a 0.05 M aqueous solution of zinc acetate was used instead of aqueous ammonia, and a 5 percent aqueous solution of non-ionic surfactant OS-20 (ethoxylated aliphatic alcohol C₁₆-C₁₈) was fed to improve dispersion stability. The total process duration was 500 min.

10

Example 5.

A dispersion was produced as in Example 2 but the feed ratio was changed, a 0.05 M aqueous solution of zinc acetate was used instead of aqueous ammonia, and a 5 percent aqueous solution of non-ionic surfactant OS-20 was introduced to improve dispersion stability. The total process duration was 535 min.

15

Example 6.

A dispersion was produced as in Example 1 but the feed ratio was changed. The total process duration was 500 min.

20

Example 7.

A dispersion was produced as in Example 2 but the feed ratio was changed, and ethylene glycol diacrylate (EGDA) was used instead of EGDM. The total process duration was 540 min.

25

Example 8.

A dispersion was produced as in Example 2 but feed the ratio was changed, and acrylic acid (AA) was used instead of MAc. The total process duration was 500 min.

30 Example 9.

Stage 1 was carried out analogous to that of the Example 1.

Stage 2

0.16 g of AP dissolved in 5 g of water was added to the dispersion prepared in Stage 1. The resulting mixture was stirred for 5 min. A monomer mixture containing 5.32 g of MMA, 11.44 g of BMA, 0.88 g of MAc and 0.09 g of EGDM, was fed over 60 min. at the rate of 0.296 g/min. An aqueous phase containing 0.08 g of AP, 0.12 g of a 37 percent aqueous solution of Elfan OS-46 and 3 g of water was prepared separately. Said aqueous phase as well as a monomer mixture containing 4.47 g of MMA, 3.98 g of BMA, 0.45 g of MAc and 0.04 g of EGDM, was fed simultaneously to the dispersion over 60 min., the rates being 0.053 and 0.149 g/min., respectively. After the feed of the aqueous phase and monomer mixture was completed, the dispersion was stirred for 30 min. at a temperature of 80°C.

Stage 3 was carried out analogous to that of the Example 2.

The total process duration was 620 min.

15 Example 10.

A dispersion was produced as in Example 1 but the feed ratio was changed, and methyl acrylate (MA) was used instead of BA. The total process duration was 500 min.

Example 11.

20 A dispersion was produced as in Example 1 but the feed ratio and conditions of Stage 1 were changed. After the primary copolymerization of the Stage 1 was completed, a monomer mixture, at the rate of 0.556 g/min., was fed to the primary dispersion instead of the monomer emulsion, 2-ethylhexyl acrylate (EHA) was used instead of BA, and allyl methacrylate (AMA) was used instead of EGDM.

25

Example 12.

A dispersion was produced as in Example 1 using monobutyl maleate (MBM) instead of MAc, and sodium dodecylbenzene sulfonate instead of Elfan OS-46.

30 Example 13.

Stage 1.

45 g of demineralized water containing 0.12 g of dissolved Elfan OS-46 was fed into 0.5 l reactor. The reactor contents were blown with nitrogen and heated to 80°C. A

monomer mixture containing 8.87 g of BA and 0.03 g of EGDM was fed into the reactor, 0.13 g of ammonium persulfate (AP) dissolved in 10 g of water was added after 5-min. stirring, and a primary polymerization process was carried out for 30 min. A solution of 0.17 g AP in 5 g of water was added to the primary dispersion, the dispersion was stirred
5 for 5 min., and a separately prepared emulsion including 79.8 g of BA, 0.24g of EGDM, 0.70 g of Elfan OS-46 and 28 g of water, was fed for 135 minutes with the rate of 0.812 g/min. After completing the addition, the dispersion was stirred for 30 min. at a temperature of 80°C.

Stages 2 and 3 were carried out analogous to those of the Example 1. The total
10 process duration was 515 min.

The preceding Examples show that aqueous heteropolymer dispersions produced according to the invention provide transparent, hard, non-tacky and high impact coatings for glass articles using a simple process unlike that of US Patent 4,009,317.

Table1

FEED COMPOSITION FOR PRODUCING AQUEOUS POLYMER DISPERSIONS
(grams)

Exam-ple	Stage	(Meth)acrylate				Di(meth)acrylate			Acid		Persulfate of			Surfactant		Water	Neutralizing/ cross-linking agent	
		MA	BA	MMA	BMA	EGDA	EGDM	AA	MAc		potas-sium	ammo-nium		Elfan	OS-20		amm-onia	Zn aceta-te
1	2	3	4	5	6	7	8	9	10		11	12		13	14	15	16	17
1	1		88.67				0.27					0.26		3.61		102		
	2			5.32	11.44		0.09		0.88			0.16				6.6		
	3			1.33	23.34				2.0			0.10		1.30		22.2	1.61	
	Total		88.67	6.65	34.78		0.36		2.88			0.52		4.91		130.8	1.61	
2	1		88.40				0.28		4.66			0.28		3.01		102		
	2			5.60	3.61		0.20		0.76			0.09				3.6		
	3			14.26	13.33				2.24			0.09		1.41		12	1.81	
	Total		88.40	19.86	16.94		0.48		7.66			0.46		4.42		70.6	1.81	
3	1		79.92				0.08					0.32		3.5		95		
	2			8.00	17.20		0.13		1.34			0.20				5		
	3			1.33	23.34				2.00			0.10		1.3		25	1.61	
	Total		79.92	9.33	40.54		0.21		3.34			0.62		4.8		125	1.61	
4	1		86.41				0.26					0.26		2.0		95		
	2			10.00	9.9		0.1					0.18				5		
	3			2.67	22.0				2.00			0.10		1.0	13.3	30		46.5
	Total		86.41	12.67	31.9		0.36		2.00			0.54		3.0	13.3	130		46.5
5	1		75.76				0.24		4.01			0.26		2.96		98.7		
	2			7.99	17.09		0.26		1.32			0.10				9.9		
	3			6.67	17.33				2.66			0.10		0.99	26.6	19.7		62.0
	Total		75.76	14.66	34.42		0.50		7.99			0.46		3.95	26.6	128.3		62.0

Table 1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
6	1		79.78		8.89		0.27				0.27	3.6		95		
	2			8.77	8.87		0.09				0.15			5		
	3				24.67				2.00		0.10	1.3		50	1.61	
	Total		79.78	8.77	42.43		0.36		2.00		0.52	4.9		150	1.61	
7	1		83.55		4.66	0.46			4.66		0.28	3.01		102		
	2			6.45	5.81	0.07			1.00		0.07			9.2		
	3			5.33	18.68				2.66		0.22	0.37		42.5	1.68	
	Total		83.55	11.78	29.15	0.53			8.32		0.57	3.38		153.7	1.68	
8	1		88.40				0.28	4.66			0.28	2.96		102		
	2			6.32	5.94		0.07	1.00			0.11			9.2		
	3			5.33	19.34			2.00			0.22	0.74		37	1.61	
	Total		88.40	11.65	25.28		0.35	7.66			0.61	3.70		148.2	1.61	
9	1		88.67				0.27				0.26	3.61		97		
	2			9.79	15.42		0.13		1.33		0.24	0.12		8		
	3				16.31				1.33		0.10	0.92		25	1.07	
	Total		88.67	9.79	31.73		0.40		2.66		0.60	4.65		130	1.07	
10	1	93.06					0.28				0.28	4.04		100		
	2			13.20	13.34		0.13				0.21			5		
	3				12.33				1.00		0.05	0.43		25	0.81	
	Total	93.06		13.20	25.67		0.41		1.00		0.54	4.47		130	0.81	
11	1		99.70 ¹				0.30 ²			0.26		0.41		97		
	2			3.32	7.14		0.06 ²		0.55	0.16				3		
	3			1.11	19.49				1.67	0.10		0.48		30	1.61	
	Total		99.70 ¹	4.43	26.63		0.36 ²		2.22	0.52		0.89		130	1.61	
12	1		88.67				0.27			0.26		3.61 ⁴		97		
	2			5.32	11.44		0.09		0.88 ³	0.16				3		
	3			1.33	23.44				2.00 ³	0.10		1.30 ⁴		30	1.61	
	Total		88.67	6.65	34.88		0.36		2.88 ³	0.52		4.91 ⁴		130	1.61	
13	1		88.67				0.27			0.26		0.82		97		
	2			5.32	11.44		0.09		0.88	0.16				3		
	3			1.33	23.44				2.00	0.10		1.30		30	1.61	
	Total		88.67	6.65	34.88		0.36		2.88	0.52		2.12		130	1.61	

Table 1 (continued)

NOTES: 1. EHA is used instead of BA

2. AMA is used instead of EGDM

3. Monobutyl maleate is used instead of MAC

4. Sodium dodecylbenzene sulfonate is used instead of Elfan OS-46

NOTATION: MA – methyl acrylate; BA – butyl acrylate; MMA – methyl methacrylate; BMA – butyl methacrylate; EHA – 2-ethylhexyl acrylate; AMA – allyl methacrylate; EGDA – ethylene glycol diacrylate; EGDM – ethylene glycol dimethacrylate; AA – acrylic acid; MAC – methacrylic acid; Elfan – 37 percent solution of Elfan OS-46 (sodium C₁₄-C₁₆ alkyl sulfonate); OS-20 – 5 percent aqueous solution of OS-20 (ethoxylated aliphatic alcohol C₁₆-C₁₈); ammonia – 24.5 percent aqueous ammonia solution; Zn acetate – 0.05 M aqueous solution of zinc acetate.

Table 2

COMPOSITION AND PROPERTIES OF DISPERSIONS AND COATINGS

Factor	Example												
	1	2	3	4 ¹	5 ¹	6	7 ²	8 ³	9 ⁴	10 ⁵	11 ⁸	12 ⁹	13
Monomer distribution between process stages, percent wt.:													
	66.7	70.0	60.0	65.0	60.0	66.7	70.0	70.0	66.7	70.0	75	66.7	66.7
	13.3	7.6	20.0	15.0	20.0	13.3	10.0	10.0	20.0	20.0	8.3	13.3	13.3
Stage 1													
Stage 2													
Stage 3													
Monomer mixture composition, percent wt.:													
Stage 1: BA	99.7	94.7	99.9	99.7	94.7	89.7	89.5	94.7	99.7	99.7	99.7	99.7	99.7
BMA						10.0	5.0						
MAc		5.0			5.0		5.0	5.0					
EGDM	0.3	0.3	0.1	0.3	0.3	0.3	0.5	0.3	0.3	0.3	0.3	0.3	0.3
Stage 2: MMA	30.0	55.0	30.0	50.0	30.0	49.5	48.5	47.5	30.0	49.5	30.0	30.0	30.0
BMA	64.5	35.5	64.5	49.5	64.0	50.0	43.5	44.5	64.5	50.0	64.5	64.5	64.5
MAc	5.0	7.5	5.0	5.0	5.0		7.5	7.5	5.0		5.0	5.0	5.0
EGDM	0.5	2.0	0.5	0.5	1.0	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Stage 3: MMA	5.0	47.8	5.0	10.0	25.0		20.0	20.0			5.0	5.0	5.0
BMA	87.5	44.7	87.5	82.5	65.0	92.5	70.0	72.5	92.5	92.5	87.5	87.5	87.5
MAc	7.5	7.5	7.5	7.5	10.0	7.5	10.0	7.5	7.5	7.5	7.5	7.5	7.5
Neutralizing (cross-linking) agent:													
type	NH ₃	NH ₃	NH ₃	Zn acetate	Zn acetate	NH ₃	NH ₃	NH ₃	NH ₃	NH ₃	NH ₃	NH ₃	NH ₃
mole COOH/mole of agent	1:0.69	1:0.29	1:0.6	1:0.1	1:0.1	1:1	1:0.32	1:0.22	1:0.50	1:1	1:0.69	1:0.69	1:0.69

Table 2 (continued)

Factor	Example												
	1	2	3	4 ¹	5 ¹	6	7 ²	8 ³	9 ⁴	10 ⁵	11 ⁸	12 ⁹	13
Size of latex particles, nanometer	Stage 1												
	Stage 2												
	Stage 3												
Solid content of the dispersion, percent wt.	50.1	49.9	50.3	40.2	37.2	46.5	45.3	46.2	50.2	50.0	50.0	50.1	48.7
pH	7.5	7.0	7.6	2.2	2.3	8.4	8.0	7.0	7.8	7.9	7.4	7.2	7.5
Viscosity after neutralization (flow time of VZ-4 viscometer), s	48.0	42.2	51.2	30.2	33.4	37.2	39.1	35.0	50.1	49.7	51.0	39.9	33.2
MFT ⁶ , °C	30.5	42.7	34.1	36.0	45.0	28.8	41.3	41.8	28.6	30.2	30.5	30.0	30.0
T _g ⁷ , °C	core intermediate shell outer shell	-53.3	-47.0	-54.3	-53.3	-47.0	-47.6	-43.5	-47.0	-53.3	-69.0	-53.3	-53.3
		51.6	85.1	51.6	60.5	53.9	60.1	71.3	70.4	60.1	51.6	51.6	51.6
		33.0	67.2	33.0	36.6	51.7	29.4	47.7	39.4	29.4	33.0	33.0	33.0
Impact tension, kJ/m ²	300	210	160	200	230	220	240	280	220	190	260	280	210
Integral light transmission, percent	91.9	92.0	91.5	91.2	91.5	91.8	91.7	91.6	91.7	91.8	91.7	91.8	91.5
Relative hardness	0.50	0.69	0.62	0.68	0.70	0.52	0.48	0.50	0.66	0.39	0.42	0.50	0.50
Adhesive strength, kN/m	0.37	0.39	0.30	0.37	0.34	0.32	0.32	0.38	0.31	0.40	0.39	0.37	0.37
Coating tackiness	n o t t a c k y												
Impact strength of article	h i g h i m p a c t w i t h o u t d e f o r m a t i o n												

Table 2 (continued)

NOTES:

1. 0.5 percent of non-ionic surfactant OS-20 (ethoxylated aliphatic alcohol C₁₆-C₁₈) is introduced additionally when cross-linking is carried out.
2. EGDA is used instead of EGDM.
3. AA is used instead of MAC.
4. Two monomer layers with different composition are formed in producing intermediate shell.
5. MA is used instead of BA.
6. Minimum film-formation temperature.
7. Glass transition temperature T_g of the copolymer is calculated using Fox equation

$$\frac{1}{T_{gt}} = \frac{q_1}{T_{gt1}} + \frac{q_2}{T_{gt2}} + \frac{q_3}{T_{gt3}} + \frac{q_4}{T_{gt4}}$$

- where q_n is mass fraction of the monomer n, T_{gm}—glass transition temperature of the polymer n.
8. EHA instead of BA, AMA instead of EGDM is used.
 9. Monobutyl maleate is used instead of MAC.

NOTATION: MA — methyl acrylate; BA — butyl acrylate; MMA — methyl methacrylate; BMA — butyl methacrylate; EHA — 2-ethylhexyl acrylate; AMA — allyl methacrylate; EGDA — ethylene glycol diacrylate; EGDM — ethylene glycol dimethacrylate; AA — acrylic acid; MAC — methacrylic acid; NH₃— 24.5 percent aqueous ammonia solution; Zn acetate — 0.05 M aqueous solution of zinc acetate.

Claims

1. An aqueous heteropolymer dispersion for manufacturing coatings, particles of the dispersion comprising copolymers that include acrylic monomer units and comprising a core and at least one outer shell, wherein: the particles comprise the core, an intermediate shell and an outer shell; a core copolymer is a copolymer of (meth)acrylate ester, or a mixture of said esters, an ethylenically unsaturated monomer containing two or three C=C bonds, and, optionally, an ethylenically unsaturated monomer containing carboxylic groups, the core copolymer having a glass transition temperature of less than 7°C; an intermediate shell copolymer is a copolymer of methacrylate ester, or a mixture of said esters, an ethylenically unsaturated monomer containing two or three C=C bonds, and, optionally, an ethylenically unsaturated monomer containing carboxylic groups, the intermediate shell copolymer having a glass transition temperature of 50 to 85°C; an outer shell copolymer is a copolymer of methacrylate ester, or a mixture of said esters, and an ethylenically unsaturated monomer containing carboxylic groups, the outer shell copolymer having a glass transition temperature of 25 to 70°C; and wherein the weight parts of the core, intermediate shell and outer shell are, respectively, 60-75, 7.5-20, and 10-22.5; and the average size of the particles is of 50 to 220 nanometers.
2. The aqueous heteropolymer dispersion of Claim 1 wherein: a (meth)acrylate ester is a compound selected from the group including compounds of the formula $\text{CH}_2=\text{CR}-\text{C}(\text{O})\text{OR}_1$, wherein R is H or CH_3 , R_1 is C_1 - C_{18} alkyl; the ethylenically unsaturated monomer containing two or three C=C bonds is a compound selected from the group consisting of: di(meth)acrylate ester of ethylene glycol, diethylene glycol, triethylene glycol, allyl (meth)acrylate, trimethylolpropane trimethacrylate, triallyl cyanurate and divinylbenzene, the ethylenically unsaturated monomer containing carboxylic groups is a compound selected from the group including acrylic acid or its α - C_1 - C_5 alkyl derivatives, as well as maleic acid, fumaric acid, itaconic acid or C_1 - C_4 alkyl monoesters thereof.
3. The aqueous heteropolymer dispersion of Claim 1 wherein: the core copolymer is a copolymer of (meth)acrylate ester or a mixture of said esters, di(meth)acrylate ester, and, optionally, (meth)acrylic acid, the copolymer containing 0.1 to 0.5 wt. percent of

di(meth)acrylate ester units and 0 to 5 wt. percent of (meth)acrylic acid units; the intermediate shell copolymer is a copolymer of methacrylate ester or a mixture of said esters, di(meth)acrylate ester, and, optionally, (meth)acrylic acid, the copolymer containing 0.5 to 2.0 wt. percent of di(meth)acrylate ester units and 0 to 7.5 wt. percent of (meth)acrylic acid units; and the outer shell copolymer is a copolymer of methacrylate ester or a mixture of said esters, and (meth)acrylic acid, the copolymer containing 7.5 to 10.0 wt. percent of (meth)acrylic acid units.

4. A process for production of an aqueous heteropolymer dispersion for manufacturing coatings, particles of the dispersion comprising copolymers which include acrylic monomer units and consisting of a core and at least one outer shell, by multistage emulsion copolymerization comprising successive stages of emulsion copolymerization of monomers for the formation of the core and shell at a temperature less than 100°C in the presence of water soluble free radical initiator and anionic surfactant, wherein: a stage of producing the core copolymer is divided into two steps, the first step including emulsion copolymerization in the presence of said initiator and said anionic surfactant by batch feeding 10 to 30 percent of the entirety of the core monomers to form an initial latex, and the second step including gradual addition of the rest of core monomers, optionally in the form of an emulsion stabilized with anionic surfactant, to the initial latex ; a stage of producing intermediate shell copolymer is carried out by feeding an intermediate shell monomer mixture to the core copolymer dispersion after introducing an aqueous solution of the initiator thereto; a stage of producing outer shell copolymer is carried out by emulsion copolymerization of outer shell monomers in the presence of the dispersion produced at the preceding stage, the outer shell monomers being either added by two equal portions after addition of aqueous solutions of the initiator and anionic surfactant or fed as an aqueous monomer emulsion stabilized by anionic surfactant with simultaneous feeding of the aqueous initiator solution which optionally contains dissolved anionic surfactant; wherein the monomer mixture of at least one stage contains an ethylenically unsaturated monomer containing carboxylic groups, and wherein an aqueous solution of at least one of ammonia, or volatile aliphatic amine, or water soluble bivalent metal hydroxide or salt, is added to the dispersion after the polymerization process is complete, the amount of the compound added being from 0.1 to 1.0 mole per mole of carboxylic group units of said ethylenically unsaturated monomer containing carboxylic groups.

5. The process of Claim 4 wherein a non-ionic surfactant is introduced into the dispersion before adding the water soluble bivalent metal hydroxide or salt, the quantity of non-ionic surfactant being from 0,5 to 1,0 percent of the copolymer weight.

5

6. The process of Claims 4 to 5 wherein the stage of producing the intermediate shell copolymer is divided into two steps, the monomer mixture compositions at these steps being different.

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7. The process of Claims 4 to 6 wherein the quantity of water soluble initiator and anionic surfactant is from 0.3 to 0.4 percent and 0.2 to 2 percent, respectively, of monomer weight when producing the core copolymer, 0.3 to 0.9 percent and 0 to 0.5 percent, respectively, of monomer weight when producing the intermediate shell copolymer, and 0.3 to 1.2 percent and 0.3 to 3.0 percent, respectively, of monomer weight when producing the outer

15

shell copolymer.

FIG. 1

